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A downsized flow set up based on multicommutation for the sequential photometric determination of iron(II)/iron(III) and nitrite/nitrate in surface water

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Abstract

In this work, a downsized flow set up designed based on multicommutation concept for photometric determination of iron(II)/iron(III) and nitrite/nitrate is surface water is described. The flow system network comprised a set of three-way solenoid valves, reaction coil and a double-channel flow cell, which were nested in order to obtain a compact and small-size instrument. To accomplish the downsizing requirement light source (LED) and radiation detection (phototransistor) were coupled to the flow cell. In order to demonstrated the effectiveness of the system, the photometer methods based on Griess reaction and 1–10-phenantroline for nitrite and iron(II) determination, respectively, were selected. Under computer control the set up provided facilities to handle four reagent solutions employing a single pumping channel, thus permitting also the determination of nitrate and iron(III) after its reduction to nitrite and to iron(II), respectively. The overall system performance was demonstrated working several days running standard solution, no significant variation of base line, linear response range and slop (less than 1%) were observed. The usefulness of the downsized system was ascertained by analyzing a set of surface water. Aiming to access the accuracy sample were also analyzed employing reference procedures and no significant difference at 95% confidence level were observed for the four analytes. Other profitable features such as analytical throughput of 40 determination per hour; relative standard deviation of 1%; linear response range between 50 and 300 $\mu g\,l^{-1}$ for nitrite and nitrate, 0.5–6.0 $mg\,l^{-1}$ iron(II) and iron(III); low reagent consumption 75 μg for nitrate/nitrite and 0.6 mg for iron(II)/iron(III) per determination; and 2.4 ml waste generation per determination were also achieved.

Keywords: Multicommutation; Flow injection analysis; Sequential determination; Iron(II)/iron(III) speciation; Nitrate/nitrite speciation; Surface water; LED based photometer

1. Introduction

Nowadays water can be considered the most precious natural asset and attention has been given to assure its quality for human consumption, and also to obtain its mitigation after industrial uses. In this instance, the governmental agencies devoted to environmental control established minimum concentration values for several chemical species and among them iron, nitrate and nitrite. In plants for water purification for human consumption it is mandatory the determination of these chemical species in the supplying source and also after the purification processing. Furthermore, chemical speciation is considered an essential parameter to attest water quality mainly in river and lakes around the cities or manufacturing plants. In this case, the correlation between iron(III)/iron(II) and nitrate/nitrite are an important parameters, which can also be considered to help decision concerning to water quality [1,2].

Analytical procedure presenting ability to carry out the determination of iron(III)/iron(II) and nitrate/nitrite should be selected to permit chemical speciation. For nitrate and nitrite the determination procedures employing ion exchange chromatography or spectrophotometry have been widely used [3,4]. The spectrophotometer method for nitrite determination based on Griess reaction presents good sensibility and robustness [5]. Nitrate after its reduction for nitrite using cadmium column had been determined employing Griess reaction [6].

The determination of iron(II) and iron(III) aiming water quality control and also chemical speciation have been carried out

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using atomic absorption spectrometry (AAS) [7], electrochemistry [8] and spectrophotometry [9]. The spectrophotometric method based on the reaction between iron(II) ions and 1–10-phenantroline has been reported as very sensitivity and robust [10]. The iron(III) can be determined after reduction to iron(II), thus a speciation accomplishment could be implemented using this methodology. The selection of the referred spectrophotometer methods for the determination of nitrate/nitrite [5,6] and iron(II)/iron(III) [10] could permit the use of common equipment, thus decreasing the support required to implement a routine task.

To attend the norms concerning to water quality [11] the number of sample to be analyzed increase with the volume of water daily processed and to attain this requirement the increase of the reagent consumption is a natural consequence. The reagent saving and lowering of waste generation are parameters, which could be pondered to select an analytical method, considering the implications associated to the environmental restriction and cost of analysis. These compromises are very difficulty to be achieved using manual procedure, nevertheless employing automatic procedures these goals could be attained mainly by resorting those based on sequential injection analysis [12,13] or multicommutation approach [14,15].

The multicommutation approach can be defined as a branch of the flow analysis technique, where the core of the flow system manifold is constituted by assembling a set of three-way solenoid valves, each one organized to work as an independent commutation unit, thus affording facilities to handle two or more chemical solutions using a single pumping channel [16,17]. Under software control, the working condition of the flow module can be modified without its reconfiguration. By exploiting these facilities automatic procedures to carry out on line sample dilution [18,19], true titration [20,21] and solvent extraction [22,23] were implemented.

In this work, one intend to develop a flow system for the determination of iron(II)/iron(III) and nitrite/nitrate in surface water using a LED base photometer. Aiming to downsizing the equipment set up the flow network will be designed based on multicommutation and integrating in the same module the detection unit comprising light source (LED), photodetector, electronic interface for signal conditioning and flow cell.

2. Experimental

2.1. Reagents solutions

All chemicals were of analytical grade. Purified water (conductivity less than 0.1 $\mu S\,cm^{-1}$) was use troughout.

A 200 $mg\,l^{-1}$ iron(III) stock solution was prepared by dissolving 1.4297 g Fe_2O_3 in 400 ml of water. After dissolution 5 ml of concentrated nitric acid was added to the solution and volume was made up to 500 ml with water. Working standard solutions 0.5, 2.0,4.0 and 6. 0 $mg\,l^{-1}$ iron(III) were prepared daily by dilution with water.A 0.25% (w/v) 1–10-phenanthroline was prepared by dissolving 0.25 g of solid in 100 ml of water.

A 1000 $mg\,l^{-1}$ nitrate stock solutions was prepared by diluting 3.0340 g of $NaNO_3$ in 500 ml of water. When not in use the solution was maintained in freezer at 4 °C. Prior to prepare the reference solutions a less concentrated solution 1.0 $mg\,l^{-1}$ NO_3^{-1} was prepared. Before using working standard solutions 50, 100, 200, 300 and 400 $\mu g\,l^{-1}$ NO_3^{-1} were prepared by appropriate dilution with water.

A 1000 $mg\,l^{-1}$ nitrite stock solutions was prepared by diluting 0.78 g of $NaNO_2$ in 500 ml of water. When not in use the solution was maintained in freezer at 4 °C. Before using working standard solutions 50, 100, 200, 300–400 $\mu g\,l^{-1}$ NO_2^{-1} were prepared by appropriate dilution with water.

The Griess reagent solution was prepared dissolving 2.0 g sulfanilamide plus 0.1 g *N*-(1-naphthyl) ethylendiamine dihydrochloride in 10 ml of a 85% (w/v) phosphoric acid solution. After dissolution the volume was made up to in 100 ml with water. This solution was stored in a dark bottle and when not used it was maintained in freezer at 4 °C. This solution could be used for 1 month. Prior to use it was equilibrated to laboratory temperature (22 °C).

A buffer solution (pH 8.5) was prepared by dissolving 85 g ammonium chloride plus 1 g disodium ethylenediamine tetraacetic acid dihydrate (EDTA) in 1000 ml of water. After dissolution pH was adjust to 8.5 using a 1 $mol\,l^{-1}$ NaOH solution. The volume was made up to 1000 with water.

Cadmium scraps coated with copper were prepared as described elsewhere [24]. In the first step, scraps were washed with a 0.1 $mol\,l^{-1}$ HCl solution. Afterwards the scraps were sequentially washed using water, a 2% (w/v) copper sulfate solution and water again. The scraps were packed into a column presenting as dimension 50 mm long and 5 mm inner diameter.

2.2. Apparatus

The equipment set up comprised a IPC4 Smatec peristaltic pump furnished with Tygon pumping tube, seven three-way solenoid valves (161T031, Nresearch), a microcomputer equipped with an interface card (PCL-711S, Advantech Corp.), a digital multimeter presenting measurement resolution of 0.1 mV and a RS232 serial interface for data communication, a homemade electronic interface [25] to match the voltage and current intensity required to drive the solenoid valves, a homemade double channel flow cell, two LED (λ = 540 nm), two phototransistor (Til78), three OP07 operational amplifiers, resistors, capacitors, reaction coils and flow line of polyethylene tubing (0.8 mm i.d.) and two T-type joint devices machined in acrylic. The double channel flow cell and the LED based photometer designed to implement this project are described below.

2.3. The detection system

In Fig. 1, it is shown a pictorial representation of the double channel flow cell that was constructed using a 2.0 mm inner diameter glass tube. The inner volume of each one was 220 μl considering also the connecting arms. It was embed between two PVC blocks, which were machined to permit coupling of LEDs and phototransistor tight to flow cell. This arrangement was designed to improvement signal measurement and to attain this subject the needful electronic network for signal gener-

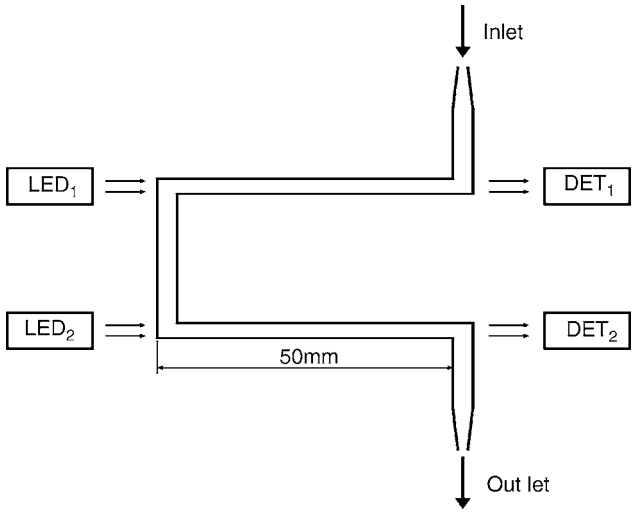

Fig. 1. Pictorial view of the double channel flow cells. LED_1 and LED_2, light emitting diode; λ, maximum at 530 nm; DET_1 and DET_2, phototransistor Til78; inlet and outlet, input and output of the solution stream, respectively.

ation and conditioning was also provided and its diagram is depicted in Fig. 2. The phototransistors (Det_1, Det_2) and the operational amplifiers (OA_1, OA_2) were assembled to form two signals transducers network where light coming from LED was converted to difference of potential. The response of each network presented linear relationships between light absorption and the concentration of the chemical specie inside of the flow cell. The network comprising the operational amplifier OA_3 was configured as an analog signal summing, therefore, the potential difference presented in its output (pin 6) was proportional to the addition of the signals coming from the operational amplifiers OA_1 and OA_2. The networks comprising the transistors (T_1, T_2) and LEDs were designed to allow the adjustment of the LEDs emission intensities by mean of the variable resistors coupled to the base of the transistors.

Prior to start the analytical run the photometer was adjusted as follow: LEDs were switched off by turning the variable resistor wired to the base of the transistors T_1 and T_2; signal output was adjusted to zero by turning the variable resistor wired to the no inverting input (pin 3) of the OA_3 operational amplifier; LED_1 was powered by turning the variable resistor and its emission intensity was adjusted to obtain a measurement of 3.000 mV in the output of the OA_3 operational amplifier; afterwards LED_2 emission intensity was adjusted to obtain 6.000 mV in the OA_3 operational output. Afterwards, the output signal was adjusted to zero by turning the variable resistor coupled to the no inverting input of the OA_3 operational amplifier (pin 3). Once accomplished the calibration step, the system could run during a workday without any additional adjustment.

2.4. The flow system

The diagram of the flow system module is shown in Fig. 3 that was designed based on the multicommutation process [26,27] to implement the analytical procedures for the determination of four analytes. The performance of the proposed flow system was dependant of the software employed to control its working sequence. Te software wrote in Quick BASIC 4.5 was developed with facilities to carry out automatically all steps involving the implemented analytical procedures. When the software was run, the flow system parameters depicted in Table 1 were displayed on the screen of the microcomputer, thus the values of the control

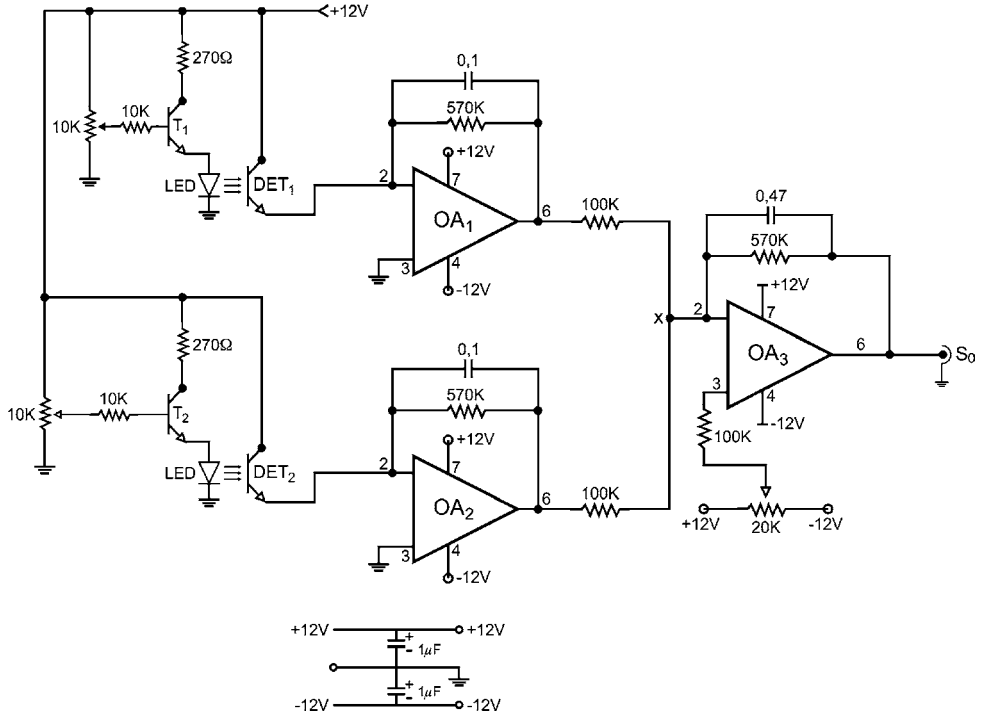

Fig. 2. Electronic diagram of the photometer. LED, light emitting diode; λ, maximum at 530 nm; DET_1 and DET_2, phototransistor Til78; OA_1, OA_2 and OA_3, OP07 operational amplifiers; T_1 and T_2, transistors BC547; S_o, signal output. Resistors and capacitors are in Ω and μF, respectively.

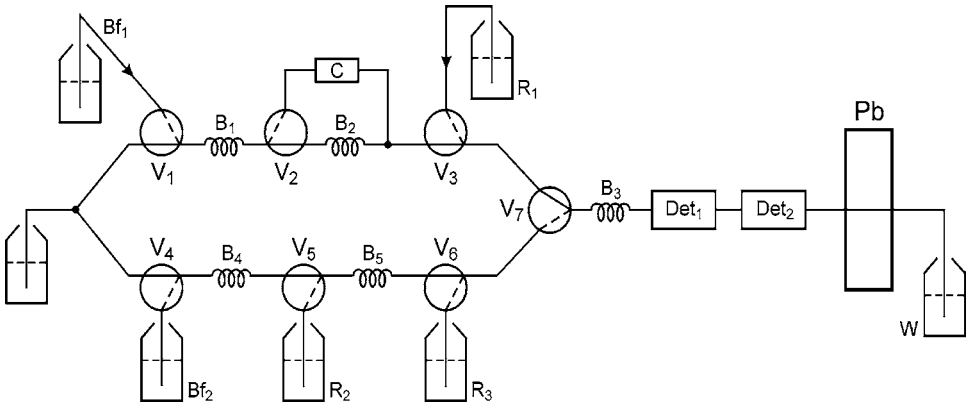

Fig. 3. Diagram of the flow system. V_1–V_7, three-way solenoid valves; B_1, B_2, B_4 and B_5, mixing coils (10 cm long, 0.8 mm inner diameter); B_3, reaction coil (100 cm long and 0.8 mm inner diameter); C, cadmium column (5 cm long and 3 mm inner diameter); Bf_1 and Bf_2, sodium borate//ammonium chloride buffer solution (pH = 9) and acetate buffer solution (pH = 4.5); R_1–R_3, Griess reagent, ascorbic acid and 1–10-phenantroline solutions, respectively; DET_1 and DET_2, photodetectors; Pb, peristaltic pump; and W, waste.

variables could be actualized. Afterwards the microcomputer run analytical procedures following the sequence established in Table 1 without any intervention of the operator.

In the configuration shown in Fig. 3, all valves are switched OFF and only sample solution (S) is flowing by suction through the valves V_1, V_2, V_3, V_7, Det_1 and Det_2 towards the waste (W). The priority established in software for the analytes determination was nitrite, nitrate, iron(II) and iron(III). In accordance with this requirement when the control software was run the microcomputer sends a set of electric pulses through the output port of the PCL711s interface card to switch ON/OFF the valve V_3.

Table 1
Sequence of the analytical run followed by the microcomputer

Analyte	Step	V_1	V_2	V_3	V_4	V_5	V_6	V_7	Time (s)
Nitrite	Sampling (a)	0	0	1	0	0	0	0	1.0
	Sampling (b)	0	0	0	0	0	0	0	0.4
	Signal reading	0	0	0	0	0	0	0	30
	Washing	0	0	0	0	0	0	0	30
Nitrate	Sampling (a)	1	1	0	0	0	0	0	1.0
	Sampling (b)	0	1	0	0	0	0	0	0.4
	Sampling (c)	0	1	1	0	0	0	0	0.4
	Signal reading	0	1	0	0	0	0	0	30
	Washing	0	1	0	0	0	0	0	30
Iron(II)	Sampling (a)	0	0	0	1	0	0	1	1.0
	Sampling (b)	0	0	0	0	0	0	1	0.5
	Sampling (c)	0	0	0	0	0	1	0	0.5
	Signal reading	0	0	0	0	0	0	1	30
	Washing	0	0	0	0	0	0	1	30
Iron(III)	Sampling (a)	0	0	0	1	0	0	1	1.0
	Sampling (b)	0	0	0	0	0	0	1	0.5
	Sampling (c)	0	0	0	0	1	0	1	0.5
	Sampling (d)	0	0	0	0	0	0	1	0.5
	Sampling (e)	0	0	0	0	0	1	1	0.5
	Signal reading	0	0	0	0	0	0	1	30
	Washing	0	0	0	0	0	0	1	30

0 indicates that valve was OFF while 1 means that the valve was switched ON. The sets of statements labeled as (a) and (b); (a), (b) and (c); (a), (b), (c), (d) and (e) are sampling cycles for nitrite, nitrate, iron(II) and iron(III), respectively. Each sampling cycles was repeated ten times.

When this valve was turned ON the sample stream was halted and reagent solution (R_1) flowed through valve V_3 towards coil B_3 and while it was switched OFF the sample stream flowed again. This ON/OFF event named as sampling cycle could be repeated several times to fill the reaction coil with a string comprising slugs of sample in tandem with slugs of reagent. When this valve was maintained OFF the sample stream flowed continuously, thus displacing the mixing of sample and reagent solution towards the detectors (Det_1, Det_2) where the analytical signal was generate.

The overall operational sequence to implement the analytical is summarized in Table 1. Because both number of sampling cycle (ON/OFF valve switching) and the time interval elapsed while valve was maintained ON could affect the sensitivity of the procedure, these parameters were the first ones that were investigated. In this sense, the number of sampling cycles was varied from 5 to 15. For nitrite determination the sampling cycles comprised two steps labeled as (a) and (b). The time interval elapsed while valve V_3 was turned ON was varied from 0.2 to 0.6 s and the time interval for it switched OFF was maintained at 0.4 s. While the string formed by sample and reagent solution slugs flowed through the reaction coil (B_3) towards the detectors (Det_1, Det_2) occurred both mixing and development of chemical reaction to form the compound that was monitored by the photodetectors. A digital multimeter was couple to the photometer output to convert the generated signal to digital and sends to the microcomputer through the serial interface. The data were saved in the hard disk as an ASCII file to permit further analysis. While sample analysis was run a signal plot was displayed on the computer screen as a time function to allow its view in real time.

Once completed the replicates programmed for nitrite, the course of the procedure was directed for nitrate determination, which was done as depicted in Table 1. In this case, valves V_1 and V_3 were ON/OFF several times (5 to 15) in order to fill the reaction coil B_1 with a mixture obtained by mixing slugs of sample and buffer solution (Bf_1). The valve V_2 was maintained ON to direct the sample zone through the cadmium column (C) where nitrate was converted to nitrite. As it is depicted in Table 1,

the sampling cycle for nitrate determination comprised three steps labeled as (a), (b) and (c). Signal measurement was carried out as described for nitrite.

After completing the run for nitrate and nitrite determination the course of work was directed to iron(II) and iron(III) determination. Valve V_7 was switched ON to direct the sample stream through valves V_4, V_5 and V_6. As it depicted in Table 1, the sampling cycle for iron(II) determination comprised three steps. Valves V_4 and V_6 were switched ON/OFF several times (five to 15) to load the reaction coil B_3 with the mixture obtained by mixing slugs of sample, buffer solution (Bf_2) and reagent solution (R_3). After ending the number of sampling cycles previously settled, the signals generated by the photometers (Det_1, Det_2) were read by the microcomputer as described for nitrate/nitrite. Afterwards, the steps for iron(III) determination were performed following the sequence settled in Table 1.

The system manifold, pumping flow rate (1.0 ml min^{-1}) and reagent concentration were maintained constant. Experiments to find the best operational conditions comprising the variation of the reagent solution volume inserted into the sample bulk was done by varying the time intervals for ON/OFF switching the solenoid valves. For iron(II) determination the ON/OFF switching pattern of the valve V_6 was studied by varying the time interval for valve turned ON from 0.2 up to 2.0 s maintaining OFF for 0.4 s. The ON/OFF switching pattern of the valve V_4 was maintained as indicated in Table 1 and number of sampling cycles was varied from 5 to 15.

Because it is necessary to insert ascorbic acid solution into the mixture of sample and buffer solution (Bf_2) prior to insert the chromogenic reagent (R_3), the sampling cycle for iron(III) determination comprised five steps as it is shown in Table 1. The valve V_5 ON/OFF switching pattern was assayed maintaining it turned OFF at 0.4 s and varying the time interval to switch ON from 0.5 up to 2.0 s. The number of sampling cycles was varied from 5 to 15. The switching pattern for valve V_6 was the same settled for iron(II) determination.

The best operational conditions of the system are summarized Table 1 and when the software was run, the microcomputer displayed the corresponding values on the computer screen and it asked if these values would be actualized or not. When it is affirmative the microcomputer waited the new values and afterwards the analytical run was carried out. Once the best operational conditions were settled a set of river water samples was analyzed in order to prove the feasibility of the proposed system and to access accuracy the samples were also analyzed employing an usual FIA procedures [28,29].

3. Results and discussion

3.1. Signal summing effect

The flow system comprised two flow cells (path length 50 mm), which were nested in tandem aiming to improve sensitivity, thus to attain this goal the measurement system depicted in Fig. 2 was designed. The signal generated by the phototransistors (Det_1, Det_2) were converted to potential difference (mV) by the operational amplifiers OA_1 and OA_2 and sent to the operational amplifier OA_3 that was configured as an analog signals summing. Under this configuration, it would be expected that the output signal (S_o) should present a linear relationship concerning to adding the signals coming from the operational amplifiers OA_1 and OA_2. In this sense, some experiments were carried out to confirm this assumption using a set of nitrite standard solution with concentration within the range of 50–400 μg L^{-1}. The corresponding linear equation, which were deduced from the obtained results are shown in Table 2. Comparing the slops of the analytical curves we can observe that an increase in signal was achieved in the adding condition, nevertheless it was 30% lower than the sum of the two slops. The sensitivity improvement was less than the expected value, nevertheless standard deviation and linearity were similar to that achieved using a single channel, and therefore this arrangement could be used to improve sensitivity.

Table 2
Linear parameters of the photometer

Detector	Linear equation	Regression (R^2)
Det_1	$V = (0.1007 \pm 0.0025) + (0.0081 \pm 0.0005)X$	0.9907
Det_2	$V = (0.3494 \pm 0.0018) + (0.0103 \pm 0.004)X$	0.9941
$Det_1 + Det_2$	$V = (1.0154 \pm 0.0027) + (0.0134 \pm 0.0006)X$	0.9895

X = nitrite concentration μg l^{-1}.

3.2. Nitrite and nitrate determination

Flow rate, reaction coils length, reagent concentration were maintained throughout, thus the variable assayed aiming to find better sensitivity was the ratio between sample and reagent aliquots inserted into the analytical path. The volume of the sample slug was maintained (66.4 μl), while the volume of the reagent solution was varied yielding the results shown in Table 3. Results obtained for nitrite were similar to those achieved for nitrate, thus they were not showed. Considering sensitivity as the main parameter better results was achieved when the volume of the reagent solution was 66.4 μl. These experiments were carried out by settling 10 sampling cycles, thus the overall volume of the sample zone varied from 960 up to 1660 μl. The volume of the analytical path comprising the volumes of the reaction coil and flow cells was 940 μl. This volume was lower than the volume of sample zone, thus minimizing dispersion effect. In this sense, variation in sensitivity in the first and second cases could be caused because reagent into the sample bulk was not enough to attain the reaction stoichiometry and in the last one it could be caused by sample dilution owing to reagent slug was higher than sample slug.

A set of river water was analyzed selecting the operational condition shown in Table 3 (line 3). To allow accuracy assessment the samples were also analyzed employing the usual FIA procedure [29] yielding the results shown in Table 4.

A applying the paired t-test for both analytes were found 2.23 while the reference value was 2.57, thus indicating that no significant difference at 95% confidence level was observed.

Table 3
Effect of the reagent volume on sensitivity

Sample slug volume (μl)	Reagent slug volume (μl)	Linear equation	Regression (R^2)
64	33.2	$V = (0.4610 \pm 0.0689) + (0.0019 \pm 0.0003)X$	0.9661
64	49.2	$V = (0.3023 \pm 0.0371) + (0.0115 \pm 0.0002)X$	0.9994
64	66.4	$V = (0.4711 \pm 0.223) + (0.0112 \pm 0.0012)X$	0.9986
64	99.6	$V = (0.4614 \pm 0.0023) + (0.0123 \pm 0.0011)X$	0.9956

X = nitrate concentration $\mu g\,l^{-1}$

Table 4
Results comparison

Sample	NO_2^- ($\mu g\,l^{-1}$)		NO_3^- ($\mu g\,l^{-1}$)	
	Proposed procedure	Reference procedure	Proposed procedure	Reference procedure
1	110.9 ± 0.1	110.8 ± 0.3	67.0 ± 0.1	65.0 ± 0.3
2	98.3 ± 0.1	98.3 ± 0.2	64.1 ± 0.1	65.01 ± 0.1
3	91.4 ± 0.2	91.4 ± 0.1	64.1 ± 0.1	63.8 ± 0.1
4	87.1 ± 0.1	86.0 ± 0.1	64.1 ± 0.1	64.1 ± 0.2
5	86.1 ± 0.1	85.6 ± 0.1	65.6 ± 0.1	66.0 ± 0.1
6	90.7 ± 0.1	92.1 ± 0.1	64.1 ± 0.1	63.9 ± 0.1
7	90.7 ± 0.1	86.9 ± 0.1	64.1 ± 0.2	63.8 ± 0.3
8	92.3 ± 0.1	92.1 ± 0.1	64.1 ± 0.1	64.2 ± 0.2
9	96.2 ± 0.2	96.2 ± 0.1	64.1 ± 0.1	64.0 ± 0.3
10	98.1 ± 0.2	98.2 ± 0.3	64.1 ± 0.2	64.1 ± 0.3

Results average of four consecutive measurements.

Other advantages such as low reagent consumption (75 μg) and reduced waste generation (1.6 ml) per determination and a sampling throughput of 40 determinations per hour were also achieved.

3.3. Iron(II) and iron(III) determination

The system operational parameter assayed to settle the best operation condition for iron(II) and iron(III) determination were the volumes of 1–10-phenanthroline and ascorbic acid solutions. Because iron(III) was determined as iron(II) after reduction with ascorbic acid, the volume of 1–10-phenantroline was the first parameter investigate, which was done by varying the time interval to switch ON/OFF valve V_4 (Fig. 3) in order to change the volume from 11.2 up to 224 μl. For iron(III) the volume of ascorbic acid was varied from 11.2 up to 224 μl. Better results were obtained when the volume of 1–10-phenantroline and ascorbic acid solutions were both 112 μl. These assays were carried out using standard solutions with concentration within the range of 2.0–10.0 mg l^{-1} iron(II) and iron(III) and linear regression coefficients $R^2 = 0.9986$ ($n = 5$) for both analytes were achieved.

The operational conditions described above were employed to analysis a set of river water, which were also analyzed using reference method [28] to allow accuracy assessment and results are shown in Table 4. Aiming to estimate accuracy the paired *t*-test was applied between results obtained with the proposed procedure and those achieved using reference method. The values found for both analytes was 0.84 and reference value was 2.75, thus indicating that no significant difference at 95% confidence level was observed (Table 5).

The flow system was designed to process sequentially nitrite/nitrate and iron(II)/iron(III) without any change on its hardware and flow rate, therefore, the sampling throughput and waste generation were equal to those estimated for nitrite/nitrate determination. The estimate reagents consumptions were 0.5 mg 1–10-phenantroline and 3.0 mg ascorbic acid per determination.

The figure of merit summarized in Table 6 shows that the proposed system presented analytical features better than those found in other flow analysis procedures [24,30], which carried using commercial spectrophotometer, therefore, the designed prototype could be an interesting option for large-scale routine analysis.

Table 5
Results comparison

Sample	Fe^{2+} (mg l^{-1})		Fe^{3+} (mg l^{-1})	
	Proposed procedure	Reference procedure	Proposed procedure	Reference procedure
1	0.61 ± 0.03	0.56 ± 0.01	1.20 ± 0.03	1.17 ± 0.01
2	0.34 ± 0.03	0.34 ± 0.01	1.35 ± 0.03	1.36 ± 0.01
3	0.45 ± 0.01	0.44 ± 0.03	1.37 ± 0.06	1.37 ± 0.06
4	0.51 ± 0.08	0.50 ± 0.01	1.37 ± 0.08	1.37 ± 0.01
5	0.91 ± 0.01	0.90 ± 0.01	1.37 ± 0.01	1.37 ± 0.01
6	0.14 ± 0.01	0.13 ± 0.02	1.37 ± 0.01	1.37 ± 0.02
7	0.45 ± 0.01	0.44 ± 0.02	1.37 ± 0.01	1.37 ± 0.03
8	0.22 ± 0.02	0.22 ± 0.01	1.56 ± 0.02	1.57 ± 0.01
9	0.36 ± 0.01	0.36 ± 0.02	1.94 ± 0.01	1.95 ± 0.02
10	0.55 ± 0.06	0.50 ± 0.05	1.37 ± 0.06	1.31 ± 0.05

Results average of four consecutive measurements.

Table 6
Figure of merit

Parameters	NO_2^-	NO_3^-	Fe^{2+}	Fe^{3+}
Linear range	50–400 μg l^{-1}	50–400 μg l^{-1}	2–10 mg l^{-1}	2–10 mg l^{-1}
Regression coefficient	$R^2 = 0.9941$	$R^2 = 0.9986$	$R^2 = 0.9986$	$R^2 = 0.9986$
Relative standard deviation	0.5	0.7	0.2	0.2
Limit of detection	18 μg l^{-1}	30 μg l^{-1}	0.5 mg l^{-1}	0.5 mg l^{-1}

4. Conclusion

The proposed flow system was able to carry out the determination of four analyte using a single pumping channel, thus proving the power of the multicommutation process, thus affording facilities to design full automatic analytical procedure using not expensive devices.

The double channel flow cell coupled to two photodetectors seems not be yet employed to improve sensitivity, therefore, the results obtained showed that this arrangement could be an useful strategy for this subject without sacrificing the system feasibility.

The equipment set up comprising flow manifold, electronic interfaces for dada generation and for solenoid valves driving presented a weight about 1.5 kg. The electronic parts were installed into a metallic box with dimension of 20 cm wide, 25 cm height and 20 cm depth. The solenoid valves ware installed at front face of the metallic box, thus permitting easily maintenance. In this sense, the downsizing requirement was achieved.

The performance of the analytical procedures comprising reagent consumption, waste generation, linear response range, standard deviation and accuracy considering the four analytes were comparable to those obtained using usual flow injection analysis, therefore proving the usefulness of the proposed downsized equipment set up.

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References

[1] S.L. Feng, Z.J. Guo, J. Fan, X.G. Chen, J.Y. Sun, Microchim. Acta 149 (2005) 61.
[2] DECRETO ESTADUAL No. 8468/1976.
[3] F. Gao, L. Zhang, L. Wang, S.K. She, Anal. Chim. Acta 533 (2005) 25.
[4] K. Suvardhan, K.S. Kumar, S.H. Babu, B. Jayara, P. Chiranjeevi, Talanta 66 (2005) 505.
[5] S. Hirata, B.V. Amma, S. Karthineyans, K. Toda, Anal. Sci. 19 (12) (2003) 1687.
[6] P. Herzsprunk, A. Duffek, K. Friese, M. de Rechter, M. Schultze, W. Von Tumpling, Water Res. 39 (2005) 1887.
[7] R.C.D. Costa, A.N. Araújo, Anal. Chem. Acta 438 (2001) 227.
[8] F.R.P. Rocha, P.B. Martelli, B.F. Reis, Talanta 55 (2001) 861.
[9] B. Sahasrabuddhey, S. Mishra, A. Jain, K.K. Verma, J. Automated Meth. Manage. Chem. 21 (1999) 11.
[10] P.B. Martelli, B.F. Reis, M. Korn, I.A. Rufini, J. Brazil. Chem. Soc. 8 (1997) 499.
[11] Conselho Nacional de Meio Ambiente (CONAMA), Edict No. 357/2005, www.mma.gov.br/port/conama/index.cfm.
[12] I.P.A. Morais, M.R.S. Souto, A.O.S.S. Rangel, J. AOAC Int. 88 (2005) 639.
[13] J.F. Van Staden, R.I. Sefan, Talanta 64 (2004) 1189.
[14] B.F. Reis, M.F. Gine, E.A.G. Zagatto, J.L.F.C. Lima, R.A. Lapa, Anal. Chim. Acta 293 (1994) 129.
[15] M. Korn, L.F.B.P. Gouveia, E. Oliveira, B.F. Reis, Anal. Chim. Acta 313 (1995) 129.
[16] G.C. Luca, B.F. Reis, Spectrochim. Acta Part A 60 (2004) 579.
[17] I.P.A. Morais, I.V. Toth, A.O.S.S. Rangel, Talanta 66 (2005) 341.
[18] E.N. Fernandes, B.F. Reis, Microchem. J. 77 (2004) 107.
[19] E.N. Fernandes, B.F. Reis, J. AOAC Int. 84 (2004) 920.
[20] E.P. Borges, P.B. Martelli, B.F. Reis, Anal. Chim. Acta 135 (2000) 179.
[21] A.P.S. Paim, C.M.N.V. Almeida, B.F. Reis, R.A.S. Lapa, E.A.G. Zagatto, J.L.F.C. Lima, J. Pharmaceut. Biomed. Anal. 28 (2002) 1221.
[22] A.L.D. Comitre, B.F. Reis, Talanta 65 (2005) 846.
[23] A.L.D. Comitre, B.F. Reis, Anal. Chim. Acta 479 (2003) 185.
[24] F.R.P. Rocha, P.B. Martelli, B.F. Reis, Anal. Chim. Acta 438 (2001) 11.
[25] A.F. Lavorante, A. Morales-Rubio, M. de la Guardia, B.F. Reis, Anal. Bioanal. Chem. 381 (2005) 1305.
[26] C.K. Pires, B.F. Reis, Quimica Nova 28 (2005) 414.
[27] J.L.F.C. Lima, J.L.M. Santos, A.C.B. Dias, M.F.T. Ribeiro, E.A.G. Zagatto, Talanta 64 (2004) 1091.
[28] J. Mortatti, F.J. Krug, L.C.R. Pessenda, E.A.G. Zagatto, S.S. Jorgensen, Analyst 107 (1982) 659.
[29] M.F. Gine, H. Bergamin, E.A.G. Zagatto, B.F. Reis, Anal. Chim. Acta 114 (1980) 191.
[30] J.Z. Zhang, C. Zelbe, F.J. Millero, Anal. Chim. Acta 438 (2001) 49.